TECHNIQUES FOR REMOVING NITROGEN AND PHOSPHORUS THROUGH CHEMICAL ADDITION

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ABSTRACT

The present paper brings to the attention of the specialists in the field the main physical and chemical techniques for removing nitrogen and phosphorus from residual waters, providing exploitation details for each technique. These techniques belong to the category of advanced sewage treatment technologies. The serious problems related to water protection led to some severe restrictions regarding the concentration level allowed in the purified effluent discharged in the natural outlets.

1. INTRODUCTION

Residual water contains a series of pollutants, among which some are removed more or less during the conventional sewage treatment stages, while others are retained for a very short time or at all in the classical sewage treatment stations. The serious problems related to water protection led to some severe restrictions regarding the concentration level allowed in the purified effluent discharged in the natural outlets, restrictions that are shown in tables 1 and 2[1, 6, 12].

Table 1. Quality restrictions for CBO_5 and O_2, in surface waters

Water characteristics	Usage categories		
	I	II	III
O_2, [mgf/dm^3], minimum	6	5	4
CBO_5, [mgf/dm^3], maximum	5	7	12

Table 2. Maximum suspension quantities, possibly discharged in outlets, according to the dilution degree

Usage categories			Dillution degrees
I	II	III	
Maximum suspension quantities [mgf/dm^3]			
20 – 40	25 – 60	30 – 100	0 – 20
40 – 100	60 – 150	100 – 250	20 – 50
100 – 300	150 – 450	250 – 750	50 – 150
300 – 1.000	450 – 1.500	750 – 2.500	150 – 500

After being mixed with residual water, the outlet water should have the pH between 6,5 – 9,0.

Identifying the existing pollutants in the mechanic-biologic discharged effluent and the effects they have on the environment is highly important in establishing the advanced treatment methods, in order to obey the quality standards in force. Table 3 shows the characteristics of residual water treated mechanic-biological, as well as the effects they have on the environment and human health.

It should be mentioned that the potential effects of residual substances existing in mechanic-biologic effluents can vary significantly. Although solid suspensions and biodegradable organic compounds are retained especially through mechanic-biologic treatment, there are some instances in which extra retaining in imposed. Initially, around mid 60's, nitrogen and phosphorous compounds from residual water discharges have triggered attention due to their effect in accelerating the lakes eutrophication and stimulating the aquatic mediums. At the moment, in the countries where the treatment of residual water is very advanced, controlling the nutrients has become a common technique of residual sewage treatment, especially in the instances of refilling the subterranean water provisions. Nitrifying the residual water is also necessary in many instances for reducing the ammonia toxicity or reducing the impact on the oxygen resources in water courses or estuaries. Beginning with the 80's, a special attention is paid to nonmetals, metals, organic compounds, halogenated compounds, pesticides, herbicides, insecticides, and volatile organic compounds, all these pollutants being considered toxic for people and aquatic environment [1, 2, 3, 11].

Although in Romania the advanced treatment of residual water has become more important in the last 10 years, in the world, a series of techniques and technologies were researched, in order to insure that a treatment station effluent has characteristics corresponding to the admitted limits established by quality standards. Globally, for over 40 years, a great diversity of treatment technologies were studied, developed and applied for retaining the pollutants from residual water (suspensions, biodegradable organic substances, pathogenic germs, nutrients, organic or inorganic compounds with cancerous, mutagen, teratogenic action or with high toxicity, refractory substances, heavy metals, dissolved inorganic substances). In table 4 are shown the means of reducing residual pollutants from residual water, through advanced treatment procedures.

Table 3. Pollutants typical for residual water treated mechanic-biologic and their effects

No	Pollutant	Effects
1	Solid suspensions	They can cause sludge deposition or can interact with the outlet.
2	Biodegradable organic compounds	They can deprive the outlets of oxygen resources.
3	Nonmetals, metals, organic compounds, halogenated compounds, pesticides, herbicides, insecticides	They are toxic for people (cancerous) and for the aquatic environment.
4	Volatile organic compounds	They are toxic for people, cancerous.
		NUTRIENTS
5	Ammoniac	It increases chlorine consumption; it can be turned into nitrates and during the treatment processes it can deprive the resources of oxygen; together with the phosphorous it leads to the development of parasitic aquatic mediums. It is toxic for fish.
6	Nitrates	It stimulates the development of algae and aquatic mediums. With children, they can cause methemoglobinemia.
7	Phosphorous	It stimulates the development of algae and aquatic mediums. It

		interferes with coagulation.
	OTHER INORGANIC SUBSTANCES	
8	Calcium and magnesium	They increase water hardening and dissolved total solids.
9	Chlorides	They give water a salty taste. They interfere with agricultural and industrial processes.
10	Sulphates	Cathartic action
	OTHER ORGANIC SUBSTANCES	
11	Surfactants	They cause foaming and interfere with coagulation.

Table 4. Means of reducing residual pollutants from residual water, through advanced treatment procedures

No	Objective	Method	Effluent type subjected to advanced treatment
1	Suspension retaining	Filtration	EM, EBD
		Screening	EBD
2	Ammoniac oxidation	Nitrification in biological stage	EM, EBD, EBND
3	Reducing the nitrogen	Nitrification/de-nitrification in biological stage	EM, EBND
4	Reducing the nitrates	Separate phase of de-nitrification in biological stage	EBND and nitrification
5	Reducing P biologically	Reducing P at water surface	AUB, EM
		Reducing P at sludge surface	NAR
6	Biological methods of N and P simultaneous retaining	Reducing P and nitrification/de-nitrification in biological stage	AUB, EM
7	Reducing N by physical or chemical methods	Flash distillation	EBND
		Chlorination at breakpoint	EBND and filtration
		Ions exchangers	EBND and filtration
8	Reducing P by chemical addition	Chemical precipitation with metallic salts	AUB, EM, EBND, EBD
		Chemical precipitation with lime	AUB, EM, EBND, EBD
9	Reducing the toxic organic components and the refractory organic substances	Adsorption on active coal	EBND and filtration
		Activated sludge – powder active coal	EM
		Chemical oxidation	EBND and filtration
10	Reducing the dissolved inorganic substances	Chemical precipitation	AUB, EM, EBND, EBD
		Ions exchangers	EBND and filtration
		Ultra filtration	EBND and filtration
		Inverted osmosis	EBND and filtration
		Electro dialysis	EBND, filtration and adsorption on coal
11	Volatile organic compounds	Volatilization and flash distillation with gas	AUB, EM

EM – effluent of mechanic treatment phase; EBD – decanted effluent of biological treatment phase; EBND – non-decanted effluent of biological treatment phase; AUB – gross residual water; NAR – recirculated activated sludge.

According to the method or the combination of methods chosen, various performances can be obtained regarding the residual pollutants retained during the advanced treatment stage. Table 5 shows the treatment levels (expressed through the concentrations of diverse residual pollutants in the "tertiary" effluent), attained with diverse combinations of procedures and operations used for advanced treatment of residual water.

Table 5. Levels of treatment attained with diverse combinations of procedures and individual operations used for advanced treatment of used water

No	COMBINATION	EFFLUENT QUALITY						
		susp. (mg/l)	CBO_5 (mg/l)	CCO (mg/l)	N total (mg/l)	$N\text{-}NH_3$ (mg/l)	phosphates (mg/l)	turbidity (NTU)
a	Activated sludge and filtration on granular environment	4-6	<5-10	30-70	15-35	15-25	4-10	0,3-5
b	Activated sludge and filtration on granular environment and adsorption on coal	< 3	< 1	5-15	15-30	15-25	4-10	0,3-3
c	Activated sludge and nitrification in a single phase	10-25	5-15	20-45	20-30	1-5	6-10	5-15
d	Activated sludge, nitrification and de-nitrif. in separate phases	10-25	5-15	20-35	5-10	1-2	6-10	5-15
e	Activated sludge and salts addition	10-20	10-20	30-70	15-30	15-25	< 2	5-10
f	Activated sludge, salts addition, nitrification, de-nitrification and filtration	<5-10	<5-10	20-30	3-5	1-2	< 1	0,3-3
g	Biologic reduction of P at water surface	10-20	5-15	20-35	15-25	5-10	< 2	5-10
h	Biologic reduction of N and P at water surface	< 10	< 5	20-30	< 5	< 2	< 1	0,3-3

According to residual pollutants that should be removed and to technical-economical analyses of solutions, there are a multitude of possible combination of procedures and individual operations.

Phosphorous and nitrogen are the main nutrients existent in the effluents treated mechanic-biologic, that are important regarding the advanced treatment. Discharges of residual water containing N and P can accelerate the lakes and accumulations eutrophication and can stimulate the development of algae and aquatic plants.

Besides the fact that they produce an unpleasant aesthetic sight, the presence of algae and aquatic vegetation can affect the use of water resources, especially when they are used as resources for water supply, fish breeding and entertainment.

Significant concentrations of N in the effluent treated mechanic-biologic can have adverse effects including the consumption of oxygen dissolved in the outlets, leading to a toxic aquatic environment, influencing the efficiency of chlorine disinfection, endangering public health and affecting the possibility of reusing the treated residual water.

Nutrients control has become an important objective regarding water quality management and treatment stations design.

2. NUTRIENTS CONTROL STRATEGIES

When choosing the nutrients control strategies it is important to establish: the characteristics of raw residual water, the type of the existing treatment station, the concentrations imposed regarding N and P for the effluent and the necessity of reducing the nutrients seasonal or permanently. Nutrients control ways can imply the introduction of an individual process for controlling a certain nutrient (for example, $Al_2(SO_4)_3$ addition for P precipitation) or can imply the integration of nutrients removing process in the biological treatment phase [6, 9]. On the method and technology chosen, depends the fulfillment of demands imposed, referring to effluent quality, flexibility in operation and cost. Initially, various types of treatment gave used chemical, physical and biological systems for quantities limiting and control or nutrients form from the treatment station effluent. The most often used methods were:

- Nitrification in biological phase for ammonic oxidation;
- Biological de-nitrification using methanol for retaining N;
- P chemical precipitation.

In recent years, a series of biological procedures were developed, centered either on individual retaining of nitrogen or phosphorous or on simultaneous retaining of N and P. These procedures were highly appreciated by specialists in the area, because massive use of chemical reagents has been eliminated or reduced substantially, with all the economical consequences resulting from these.

2.1. Nitrogen control and removal

In untreated residual water, N is found as ammoniac or organic nitrogen, both soluble, as micro-particles. Soluble organic nitrogen is often found as urea or amino acids.

Table 6. The effect of different operations and treatment procedures on nitrogen based compounds [8, 10]

	Treatment operation or procedure	N based compounds			N total retained* %
		N organic	NH_3-NH_4^+	NO_3^-	
	CONVENTIONAL TREATMENT				
1	Mechanic treatment	10–20%	no effect	no effect	5–10%
2	Biologic treatment	15–50%**	< 10%	small effect	10–30%
	BIOLOGIC TREATMENT				
1	Bacterial assimilation	no effect	40–70%	slab	30–70%
2	De-nitrification	no effect	40–70%	80–90%	70–95%
3	Nitrification	limited effect	$\rightarrow NO_3$	no effect	5–20%
4	Oxidation ponds	partial transformation in NH_3-NH_4^+	partially reduced through flash distillation	partially reduced through nitrification /de-nitrification	20–90%
	CHIMICAL PROCEDURES				
1	Chlorination at breakpoint	uncertain	90–100%	no effect	80–95%
2	Chemical coagulation	50–70%	small effect	no effect	20–30%
3	Ions exchangers selective for ammoniac	small, uncertain	80–97%	no effect	70–95%
4	Ions exchangers selective for nitrates	small effect	small effect	75–90%	70–90%

5	Adsorption on coal	30–50%	small effect	small effect	10–20%
PHYSICAL OPERATIONS					
1	Filtration	30–95% from N organic in suspension	small effect	small effect	20–40%
2	Flash distillation	no effect	60–95%	no effect	50–90%
3	Electro dialysis	100% for N organic in suspension	30–50%	30–50%	40–50%
4	Inverted osmosis	60–90%	60–90%	60–90%	80–90%

* according to the initial concentration in N total of influent.

** soluble organic N, as urea or amino-acids, it is reduced substantially through the secondary treatment phase.

Untreated residual water contains less or at all nitrites or nitrates. A part of organic particles are retained by primary decantation [2, 7]. During the biological treatment, the most numerous particles containing substances based on organic nitrogen are transformed in ammonic or other organic forms. A part of ammoniac is assimilated in the biomass cells. The greatest part of N from secondary effluent is found as ammonic. In table 1 is shown the effect of different operations and treatment procedures on organic nitrogen, ammoniac and nitrates found in residual water.

2.2. Phosphorous control and removal

For most part of residual water, around 10% of P concentration corresponding to the insoluble part, is normally retained through primary decantation.

Table 7. The effects of different treatment operations and procedures on retaining phosphorous

	Treatment operations or procedures	P reduction in system, %
CONVENTIONAL TREATMENT		
1	Mechanical treatment	10 – 20%
2	Activated sludge	10 – 25%
3	Bio-filters	8 – 12%
4	Biological filters with discs	8 – 12%
BIOLOGIC REDUCTION OF PHOSPHOROUS		
1	P reduction on water surface	70 – 90%
2	P reduction on sludge surface	70 – 90%
COMBINED BIOLOGIC REDUCTION OF NITROGEN AND PHOSPHOROUS		
1	Combined biologic reduction of N and P	70 – 90%
CHEMICAL REMOVAL		
1	Salt precipitation	70 – 90%
2	Lime precipitation	70 – 90%
PHYSICAL REMOVAL		
1	Filtration	20 – 50%
2	Inverted osmosis	90 – 100%
3	Adsorption on coal	10 – 30%

Exception for the quantities incorporated in the cellular tissue; in biological phase, the reduction is minimum, because P, present in residual water after primary sedimentation, is soluble. Table 7 shows the effects of conventional treatment or other treatment procedures regarding P reduction [1, 3, 4, 5].

P removal can be done through physical, chemical and biological means. Chemical precipitation (using Fe and Al salts, or lime) has already been used for P reduction. The biological treatment methods are based on simulating the microorganisms which will take more P than needed for cellular development. Lately, the development and application of biologic techniques for reducing P was preferred, instead of chemical precipitation.

When obtaining an effluent with low concentrations regarding P (generally under 1 mg/l) is necessary, filtration is used in combination with other biologic or chemical procedures. Other physical procedures, such as ultra-filtration and inverted osmosis are important in retaining P but are still applied, for removing the dissolved inorganic substances.

2.2.1. Phosphorus removal from residual waters using biological means

Lately, a special attention was paid to procedures for P removal using biological means, as alternative to chemical methods. P is retained in biological phase through incorporating procedures of orthophosphates, polyphosphates, and phosphorous linked organically in cellular tissue [1].

Total quantity of P removed is done according to the decanters produced effectively. P contained in cellular tissue is 5 times lower than N content in tissue.

According to local environment conditions, real P matter is 7 to 3 times lower than N content from cellular tissue. On average, the quantity of P removed during secondary treatment through residual sludge can vary between 10-30% from influent quantity.

By using a biologic procedure for removing P, significant results can be obtained, outside this domain.

The concept of removing P by biologic methods means exposing the microorganisms to alternative anaerobe and aerobe conditions.

Exposition to alternant conditions determines microorganisms overstressing, so that the adsorption quantity exceeds normal levels. P is used not only for survival, synthesis and energy but it is also stored and used afterwards by microorganisms.

Sludge containing p in excess is either residual or removed in the lateral treatment flux (sludge line). Alternative exposition to anaerobe and aerobe conditions can be achieved either on water surface, or in the sludge recirculation process [2].

Specific procedures of biologic treatment used for P removal are:

- A/O procedure – which implies P removal on water surface, in biologic phase;
- PHOSTRIP procedure – implies P removal on sludge surface;
- Sequential tank procedure (B.S.) – used for small quantities of residual water, on condition that is has functional flexibility, it allows retaining N and P.

A/O procedure (retaining P on water surface) [1]

A/O procedure (fig. 1) is used for retaining P combined with C oxidation from residual water. It is a biomass system in suspension „single-sludge" (a single tank, so single sludge), which combines consecutive anaerobe and aerobe areas.

For nitrification, the supply can be done by increasing the retention time needed in aerobe area. The sludge deposited is returned in the influent at the end of the tank and mixed with influent residual water.

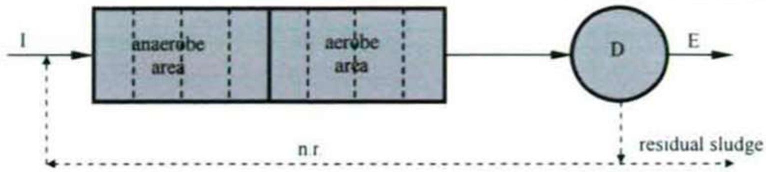

Figure 1. Technological diagram for A/O procedure:
I – influent; D – decanter; E – effluent; n.r. – recirculation sludge

Under anaerobe conditions, P contained in residual water and in the recirculated cellular mass is released as soluble phosphates. At this stage reducing partially the organic substances (as CBO_5) can be done. P is absorbed by the cellular mass in the aerobe area and is retained from fluid flow capacity into the activated sludge. P concentration in the effluent depends greatly on the ratio CBO_5 : P of residual water.

For ration higher than 10 : 1, concentrations of P soluble in the effluent under 1 mg/l can be obtained. When the ratio values are lower than 10 : 1, metallic salts should be added for obtaining low concentrations of effluent in P.

Phostrip procedure (removing P on sludge line) [1]

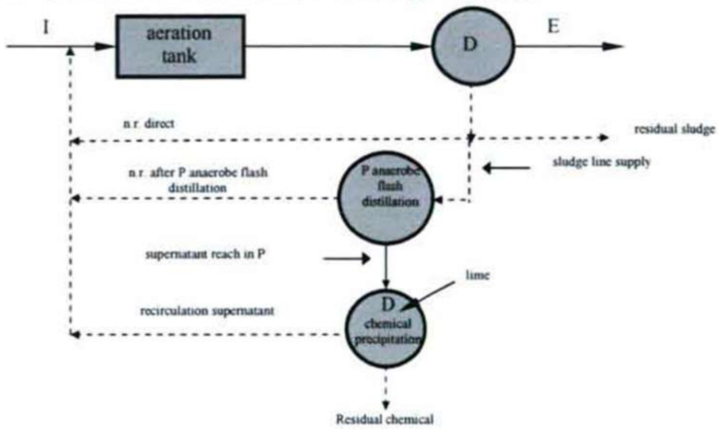

Figure 2. Technologic diagram for Phostrip procedure:
I – influent; D – decanter; E – effluent

In this procedure (fig. 2), a part of recirculated activated sludge form biologic treatment is led in an anaerobe tank for P flash distillation. The retention time in this tank generally varies between 8 and 12 hours. P is released in the flash distillation tank, it gets out of the tank as supernatant and the activate sludge poor in P is returned in the aeration tank. Supernatant reach in P is combined with lime or other coagulant in a separate tank and it is unloaded in DS or in a separate flocculation decanting tank to separate solid suspensions. P is removed from the system through chemical precipitation. PHOSTRIP type systems associated with activated sludge ones can insure an effluent with a total content of P under 1,5 mg/l, before filtration.

Procedure with sequential functioning tanks

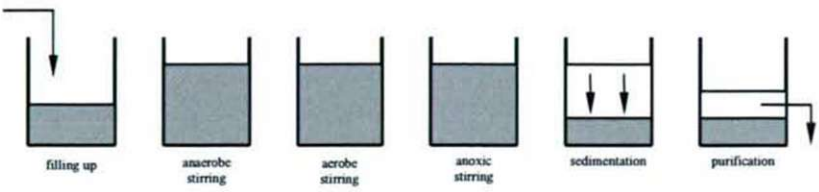

Figure 3. System with sequential loading tanks

The system (fig. 3) can operate so that it insures any combination of C oxidation with N reduction and P removal. A simple representation of this system is shown in the figure above.

3. CONCLUSIONS

Advantages and disadvantages of biologic alternatives for removing phosphorous

Below is shown a general comparison of alternative procedures for removing P using biologic means [4]. Biologic methods provide more advantages regarding the integration in the nutrients removal process in the treatment stations. Because a great part of the procedures success depends on specific local conditions, it is recommended that pilot stations tests should be performed.

A/O procedure (retaining P on water surface)

Advantages: Relatively simple functioning compared to other procedures. Residual sludge has a relatively high concentration of P 3-5% and a fertilizing value. Hydraulic retention time relatively short. In cases when only a part of P should be reduced, it can be supplemented with nitrification.

Disadvantages: It does not have the capacity to ensure separately the removal of some big quantities of N and P. Questionable performances of operation at low temperatures. It needs high values of CBO_5: P ratio. Together with minimizing the retention time of cells in the aerobe medium, a higher value of oxygen transfer might be needed. Limited flexibility in operation.

Phostrip procedure (removing P on sludge line)

Advantages: It can be incorporated in the treatment stations with existent n.a. Flexible process. P removal process is not restricted by CBO_5: P. ratio. There are many installations like this in the USA. Significant lower consumption of chemical reactives than needed for chemical precipitation in biologic phase. It can lead to orthophosphates concentrations of effluent, under 1,5mg/l.

Disadvantages: It needs lime addition for P precipitation. It needs a high concentration of O_d mixture to prevent P release in the final decanter. Cleaning the lime deposits can be considered a maintenance problem.

Procedure with sequential functioning tanks

Advantages: The process is very flexible for combining N with P removal. The process is simple. The suspensions from the mixture should not be washed in the opposite direction of hydraulic flow.

Disadvantages: Convenient only for small flows. Extra units are needed. The effluent quality depends on the decantation easiness. The design data available are limited.

Reducing these constituents can be achieved with or without chemical addition when changing the tank's functionality. P can be removed by chemical addition with coagulation reactives or biologically, without coagulation reactives addition [3]. In the configuration shown above, releasing P and reducing CBO_5 can take place during anaerobe mixing phase and reducing P in the next phase of aerobe mixing. Modifying the reaction time, nitrification or N removal can be obtained. A complete cycle total time can vary from 3 to 24 hours. In anoxic phase, a source of C as support for de-nitrification is needed, represented either by an external source, or by endogen respiration of existing biomass.

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